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HPLC MONITORING OF GRAPHITE-EPOXY PREPREG AGING.(U)
MAY 79 G L HAGNAUER, J M MURRAY, B M BOWSE

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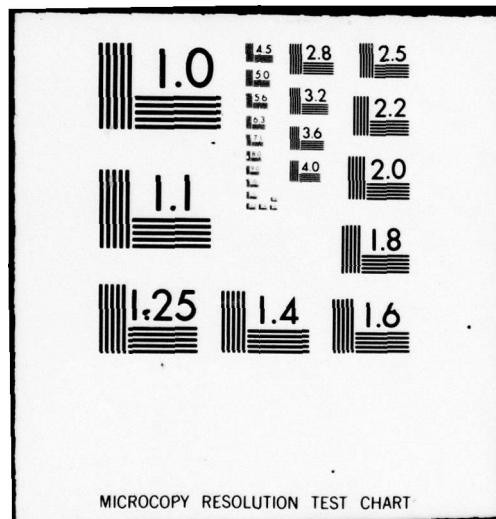
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HPLC MONITORING OF GRAPHITE-EPOXY PREPREG AGING

May 1979

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ABSTRACT

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A method using high performance liquid chromatography has been developed for the quality control of graphite-epoxy prepregs. The method may be applied both as a standard test method in Military Specifications and as a method for process control. The method is used to monitor compositional changes as the prepreg ages at -13 C, 22 C, and 49 C. Chemical changes in the prepreg are correlated with aging time and process acceptability. ↗

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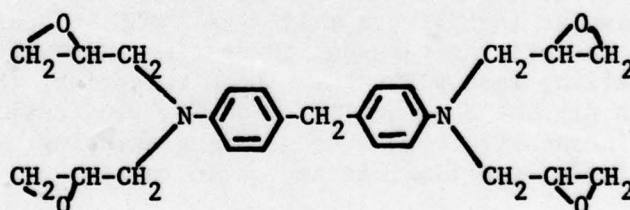
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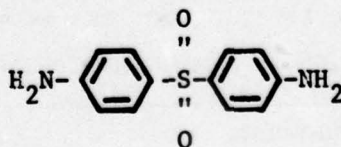
INTRODUCTION

This report illustrates the potential of high performance liquid chromatography (HPLC) as a technique for the quality control of epoxy resin preregs. Epoxy resin preregs are complex chemical systems comprised of one or more epoxies, curing agents, catalysts or accelerators, rubber modifiers, diluents, and glass or graphite fibers. To ensure fiber impregnation and prepreg integrity during the lay-up procedure and processing, resin components in most preregs are partially reacted, or B-staged, during prepreg manufacture. Thus, B-staging alters chemical composition, increasing the variety of chemical components and the difficulty of precise chemical analysis. And since the chemistry of a prepreg system ultimately controls its processability and the properties of the composite material, the more desirable monitoring or quality control methods are those which fingerprint chemical composition and permit direct analysis of specific prepreg components. HPLC is ideal for such an application. Nearly any prepreg component that can be rendered soluble can be analyzed by HPLC. A variety of HPLC techniques and conditions may be employed to optimize the separation and detection of chemical species. In this report, gel permeation chromatography (GPC) and normal phase adsorption chromatography with gradient elution are used to fingerprint and quantitatively analyze soluble prepreg components.

The Hercules 3501-6/AS graphite-epoxy prepreg has been selected for analysis for several reasons. First, quantitative information is available regarding the chemical formulation of 3501-6 prior to B-staging.¹ The prepreg contains about 60% by weight graphite fiber.² The resin formulation consists of about 56.5% weight CIBA MY720 epoxide, 24.9% weight CIBA Eporal curing agent, 1.13% weight boron trifluoride complex catalyst, plus 17.5% weight other epoxide components. The primary component (70 to 75% wt) of CIBA MY720 is N,N,N',N'-tetraglycidyl methylene dianiline (TGMDA).



CIBA Eporal is 4,4' -diamino diphenyl sulfone (DDS)



1. CARPENTER, J. F. *Assessment of Composite Starting Materials: Physicochemical Quality Control of Prepregs*. AIAA/ASME Symposium on Aircraft Composites, San Diego, CA, March 1977.
2. SANJANA, Z. N. *Overage Indicator For Graphite Fiber Epoxy*. Final Report for June 1977-June 1978, Westinghouse R&D Center Pittsburgh, PA, Naval Air System Command, Contract No. N00019-77-C-0247, June 1978.

Secondly, the constituents of 3501-6 are similar to those in other 350 F cure preregs (e.g., NARMCO 5208) for which liquid chromatographic methods have been developed.³ Finally, a definitive quality control method is needed not only for certification of preregs in procurement but also because the preregs undergo extensive "aging" at room temperatures, i.e., the preregs start turning brittle after one week and become unacceptable for processing after two or three weeks.² Little information is available regarding the chemical processes accompanying the aging or the extent to which such processes must occur for the prepreg no longer to be acceptable.

Compositional changes in the 3501-6 prepreg as it ages at -13 C, 22 C, and 49 C are monitored using HPLC. Fingerprints are obtained using different modes of liquid chromatography and comparisons are made. A major reaction product is identified and quantitatively analyzed along with the reactants TGMMA and DDS. A large number of measurements are made and treated statistically to ascertain the significance of the data. Additionally, the results of the liquid chromatographic analysis are related to prepreg processability with the aid of time/temperature monitoring devices.² Chemical changes in the prepreg are correlated with aging time and are related to processing acceptability.

EXPERIMENTAL

Hercules 3501-6/AS graphite-epoxy prepreg samples were provided by Dr. Z. N. Sanjana (Westinghouse Electric Corp., R&D Center, Beulah Road, Pittsburgh, PA) in coordination with a project sponsored by the Naval Air Systems Command, Washington, DC. The prepreg consists of unidirectional A-type graphite fiber impregnated (without solvent) with a slightly B-staged epoxy resin mixture.² The formulation of the prepreg is unknown except that it consists of CIBA MY720 as the principal epoxy component, of two other epoxides in lesser concentrations, of diaminodiphenyl sulfone (DDS) as the curing agent, and of a BF₃ accelerator.² Single-ply prepreg samples (6×6") were mailed to AMMRC in sealed packages under dry ice. Along with the prepreg samples, three time/temperature watches (TTW) activated prior to mailing were also sent. Upon reception, the sample packages were still encased in dry ice and the TTWs read "0," indicating that the samples were not exposed to inordinate temperatures during shipping. It is noted that the samples, as received, were flexible and quite tacky.

Prepreg aging was monitored at three different temperatures over extended periods of time (Table 1). The physical appearance of the prepreg, as well as the TTW reading, was recorded at each sampling. The panels stored at -13 C remained essentially unchanged in appearance over a 10-month period. However, at 22 C the prepreg became more brittle and less tacky with increasing time

Table 1. PREPREG AGING CONDITIONS

Temperature, deg C		Total Sampling Period
- 13	in a freezer	10 months
22.0 ± 0.5	on shelf in laboratory	53 days
49 ± 2	in an oven	7 days

3. HAGNAUER, G. L., SPROUSE, J. F., SACHER, R. E., SETTON, I. and WOOD, M. *Evaluation of New Techniques for the Quality Control of Epoxy Resin Formulations*. Army Materials and Mechanics Research Center, AMMRC TR 78-8, January 1978.

(Table 2). In processing 3501-6 preregs, it has been determined that the preregs are no longer acceptable when the TTW reading reaches 5 or 6 (Watch #T33) or after about 2 or 3 weeks aging at ambient temperatures; 49 C the prepreg rapidly loses tack and is no longer acceptable for processing after 2 days.²

Time/temperature watches are inexpensive time-temperature integrating and indicating devices available from the Info-Chem Division of Akzona, Inc.* A TTW is a cellophane package consisting of a strip of sensitized paper with a small glass ampoule of liquid at one end. The paper strip is scaled in units from 0 at the ampoule end to 10 at the other end. After the TTW is activated by breaking the ampoule, the liquid diffuses along the paper strip causing a color change. The rate of migration increases with temperature and the TTW responds in a reproducible and fairly linear fashion with time. At 22 C, the T30 watch has a lifetime of about one week while the T33 watch will run about two months. The X21 watch is more sensitive to temperature and therefore is used for monitoring preregs during shipping or freezer storage.

A Waters ALC/GPC-244 instrument, with 6000A solvent delivery system, U6K injector, 660 solvent programmer, 440 dual wavelength UV absorbance detector, and R400 differential refractometer (RI), was used for the HPLC analyses. A Spectra Physics SP4000 data system with SP4020 data interface and SP4050 printer/plotter was used for peak integration and data formatting. Distilled in glass 2,2,4-trimethylpentane (C8) was obtained from Burdick & Jackson Labs, Muskegon, MI. Tetrahydrofuran (THF), chloroform (CHCl₃), and water were distilled just prior to solution preparation and analysis. All solvents and solutions were filtered through 0.45 micron Millipore filters. Prepreg solutions were prepared by cutting sections (ca. 0.28 gram) off prepreg panels, weighing the sections, and dissolving the resin off the fibers in 50-ml volumetric flasks filled to the mark with solvent. The flasks were agitated and at least 30 minutes were allowed for complete dissolution. Other than the fibers, no insolubles were evident in the prepreg initially or after extended periods of aging. Commercial DDS and purified (96%) TGMDA were used as standards.

Table 2. PREPREG AGING AT 22.0 ± 0.5 C

Time (days)	TTW Readings		Comments
	T30	T33	
0	0	0	Prepreg flexible, tacky
1	2	0	Prepreg flexible, tacky
4	6	0	Prepreg flexible, tacky
5	7		Prepreg losing tack
6	8	0.2	Prepreg losing tack
7	9		Prepreg losing tack
11			Prepreg becoming brittle
15		1.8	Prepreg becoming brittle
28		4.3	Prepreg becoming brittle
33		5.4	Prepreg no longer acceptable
53		9.5	Prepreg no longer acceptable

*P.O. Box 899, Fairfield, NJ.

For gel permeation chromatography, four μ Styragel columns (30 cm \times 7.8 mm ID) having porosities of 500, 500, 100, 100A were used with CHCl_3 and also with THF as the mobile phase. The flow rate was 2.0 ml/min and standard injection volume was 50 μ l. Effluents were monitored with the UV absorbance detector at 2 AUFS and an RI detector sensitivity of 18X.

Normal phase adsorption HPLC was performed with gradient elution using two μ Porasil columns (30 cm \times 3.9 mm ID). The mobile phase was programmed linearly (Gradient 6) from (50/50) C8/THF to 100% THF over a period of 20 minutes at a flow rate of 2.0 ml/min. The standard injection volume was 15 μ l and effluents were monitored using 254 nm and 280 nm UV detectors at 2 AUFS. Data system parameters were adjusted to optimize integration for the quantitative analyses of TGMDA and DDS.

The weight percentage TGMDA or DDS in the formulated resin portion of the prepreg was calculated using the relation

$$\% \text{ wt} = \frac{A \times K_{\text{std}}}{C \times V \times 0.4} \times 100\%, \quad (1)$$

where

$$K_{\text{std}} = C_{\text{std}} \times V_{\text{std}} / A_{\text{std}}$$

is a constant determined each day prior to prepreg analysis with a standard TGMDA or DDS solution of concentration C_{std} ($\mu\text{g}/\mu\text{l}$), an injection volume V_{std} (μl), and peak area A_{std} (mV-sec). Similarly, the symbols C, V, and A represent concentration (ca. 5.6 $\mu\text{g}/\mu\text{l}$), injection volume (15 μl), and the area of the TGMDA or DDS peak in the prepreg analysis. It is assumed that 40% of the 3501-6 prepreg by weight is the formulated resin, hence 0.4 appears in the denominator. Errors were estimated by sampling from several prepreg panels and by running multiple analyses.

RESULTS

Compositional changes in the 3501-6 prepreg may be fingerprinted and monitored, at least partially, using GPC. Figure 1 compares the GPC fingerprints of 3501-6 in CHCl_3 solution after 1 day and 40 days aging at 22 C. The elution time for TGMDA is 13 minutes, whereas DDS elutes 18 minutes after injection. The peak eluting just before TGMDA represents TGMDA dimers, trimers, and higher oligomers of TGMDA and other epoxies, as well as reaction products due to B-staging. As shown in Figure 1, the concentration of unreacted DDS decreases with prepreg aging. Upon analysis, DDS is found to decrease from 23% at 1 day to 14.1% after 40 days at 22 C. The concentration of TGMDA does not appear to change over the same time period. Rather the TGMDA peak broadens and merges with the oligomer peak, TGMDA was not analyzed since its peak could not be fully resolved and since it seemed likely that other components were contributing to its peak area.

The GPC chromatograms in Figure 2 give a clearer indication of the effects of aging. In this case, THF is the solvent and the effluent is monitored using RI rather than UV detection. Obviously, solvent selection is a critical factor in the type of separation achieved. TGMDA and DDS are no longer resolved. Both components elute at about 16 minutes with DDS slightly preceding TGMDA. But

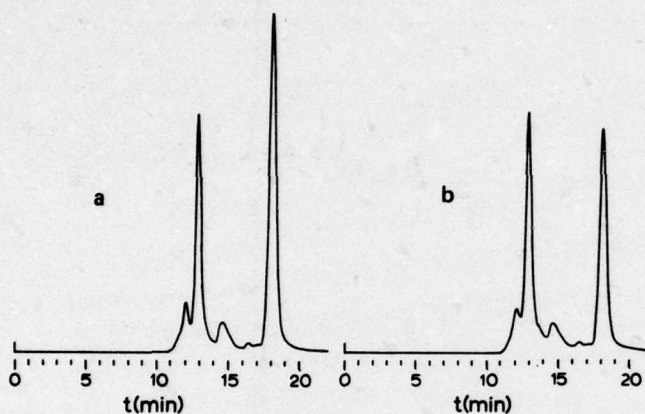


Figure 1. GPC analysis of prepreg with CHCl_3 and 254 nm UV detection. Prepreg aged at 22 C for (a) 1 day and (b) 40 days.

better resolution is achieved for the higher molecular weight components eluting between 11.5 and 15 minutes. Even though quantitative analysis is not feasible, the GPC fingerprints are quite useful since they show how the relative size and amount of higher molecular weight species increase with prepreg aging.

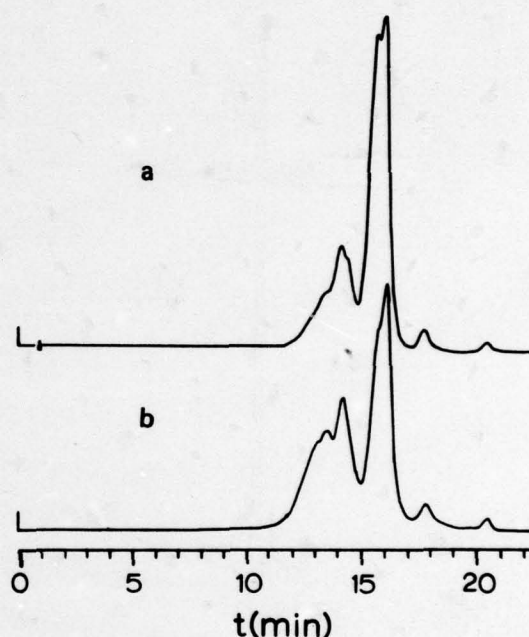


Figure 2. GPC analysis of prepreg with THF and RI detection. Prepreg aged at 22 C for (a) 1 day and (b) 40 days.

More definitive fingerprints and better resolution of unreacted DDS and TGMDA are obtained by normal phase adsorption chromatography with gradient elution. As shown in Figures 3 and 4, TGMDA and DDS have retention times of about 314 and 608 seconds. Retention times are printed in seconds after each peak. Capacity factors k' , defined as the ratio of the solute concentration in the stationary to the mobile phase, are given in Table 3. The capacity factor relates the equilibrium distribution of a solute within a column to the thermodynamic properties of the column and is evaluated from the retention times of the solute t_r and of an unretained component t_u

$$k' = \frac{t_r - t_u}{t_u} \quad (2)$$

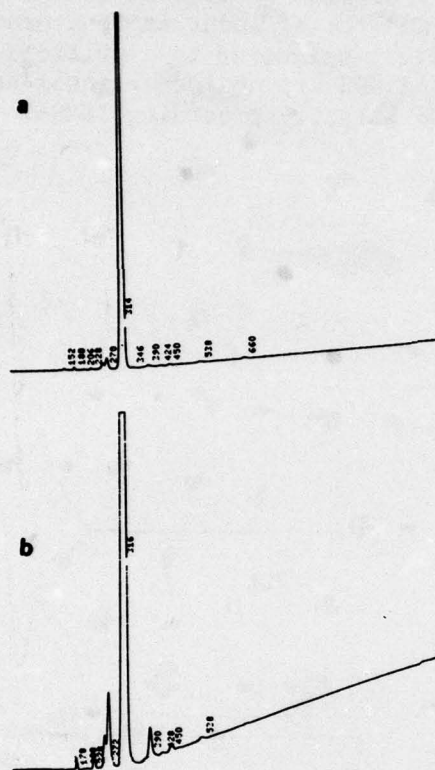


Figure 3. HPLC analysis of TGMDA with UV detection at (a) 280 nm and (b) 254 nm.

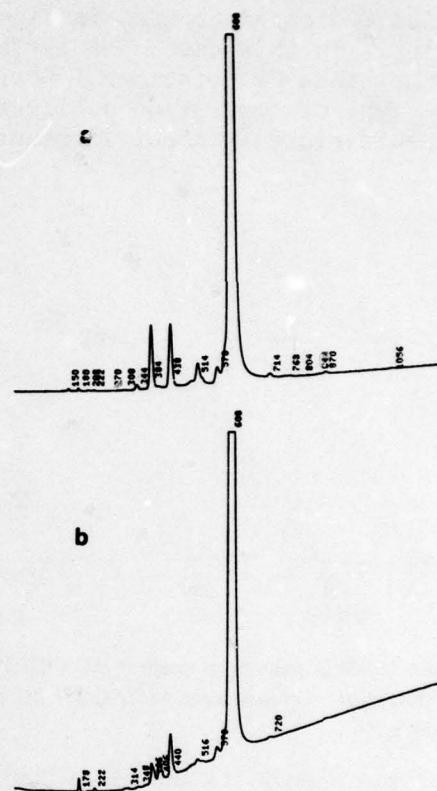


Figure 4. HPLC analysis of DDS with UV detection at (a) 280 nm and (b) 254 nm.

Table 3. HPLC PARAMETERS - NORMAL PHASE ADSORPTION

Component	k'	A_{280}/A_{254}	$k(\mu\text{g}/\text{mV}\cdot\text{sec})$	
			280 nm	254 nm
TGMDA	0.77	0.156	3.56×10^{-2}	5.57×10^{-3}
DDS	2.42	1.21	4.15×10^{-3}	5.00×10^{-3}
Product	3.35	0.51	1.02×10^{-2}	5.37×10^{-3}

Ideally, components of interest should have k' values in the range between 1 and 10. It is also evident that the molar absorptivity of TGMDA is significantly greater at 254 nm than at 280 nm, whereas DDS has a greater absorbance at 280 nm than at 254 nm. Absorbance ratios A_{280}/A_{254} , as well as calibration constants, are given in Table 3.

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HPLC fingerprints of the 3501-6 prepreg as received and after 1 and 2 days aging at 49 C are shown in Figure 5. Absorbance ratios A_{280}/A_{254} for the 314 sec and 608 sec peaks are identical to the values obtained with the TGMDA and DDS standards. This means that it is unlikely that other components which may be present in the prepreg have the same retention times as TGMDA and DDS and are contributing to their peak areas as determined by UV absorption at 254 nm and 280 nm. All peaks with retention times of 610 sec or less are attributable to DDS and to MY720 components. Essentially all the peaks having longer retention times are products formed during prepreg staging and/or as the prepreg ages.

A significant peak is observed at 778 sec. The component(s) producing this peak has a greater UV absorbance at 254 nm than at 280 nm and is denoted as "Product" in Table 3. The size of the Product peak and other peaks at higher retention times increase as the prepreg ages not only at 49 C but also at 22 C and -13 C. Preparative LC techniques were used to isolate the product component. The product was identified using Fourier transform infrared spectroscopy as a reaction product between TGMDA and DDS. The proportion of the two reactants in the product structure was determined indirectly from the product's UV absorbance ratio ($A_{280,p}/A_{254,p}$) and the calibration constants for TGMDA and DDS in Table 3. Assuming that the reaction between TGMDA and DDS does not change the contribution of either chromophore to the molar absorptivity of the product at 254 nm or at 280 nm, absorbances should be additive such that

$$A_{254,p} = xA_{254,TGMDA} + (1-x)A_{254,DDS}$$

and

(3)

$$A_{280,p} = xA_{280,TGMDA} + (1-x)A_{280,DDS}$$

where x is the fraction of TGMDA incorporated in the Product molecule. Since Eq. 3 may also be written in terms of peak areas, the calibration relation $A=CV/K$ may be substituted into the equation to give

$$K_{254,p}^{-1} = xK_{254,TGMDA}^{-1} + (1-x)K_{254,DDS}^{-1}$$

and

(4)

$$K_{280,p}^{-1} = xK_{280,TGMDA}^{-1} + (1-x)K_{280,DDS}^{-1}$$

Furthermore,

$$A_{254,p} K_{254,p} = A_{280,p} K_{280,p} \quad (5)$$

since the amount of Product calculated from data obtained at the two wavelengths must be the same. Upon replacing $K_{254,p}$ and $K_{280,p}$ by the appropriate constants in Eq. 4 and by rearrangement

$$x = \frac{K_{280,DDS}^{-1} - (A_{280,p}/A_{254,p}) K_{254,DDS}^{-1}}{(A_{280,p}/A_{254,p}) (K_{254,TGMDA}^{-1} - K_{254,DDS}^{-1}) - K_{280,TGMDA}^{-1} + K_{280,DDS}^{-1}} = 0.69 \quad (6)$$

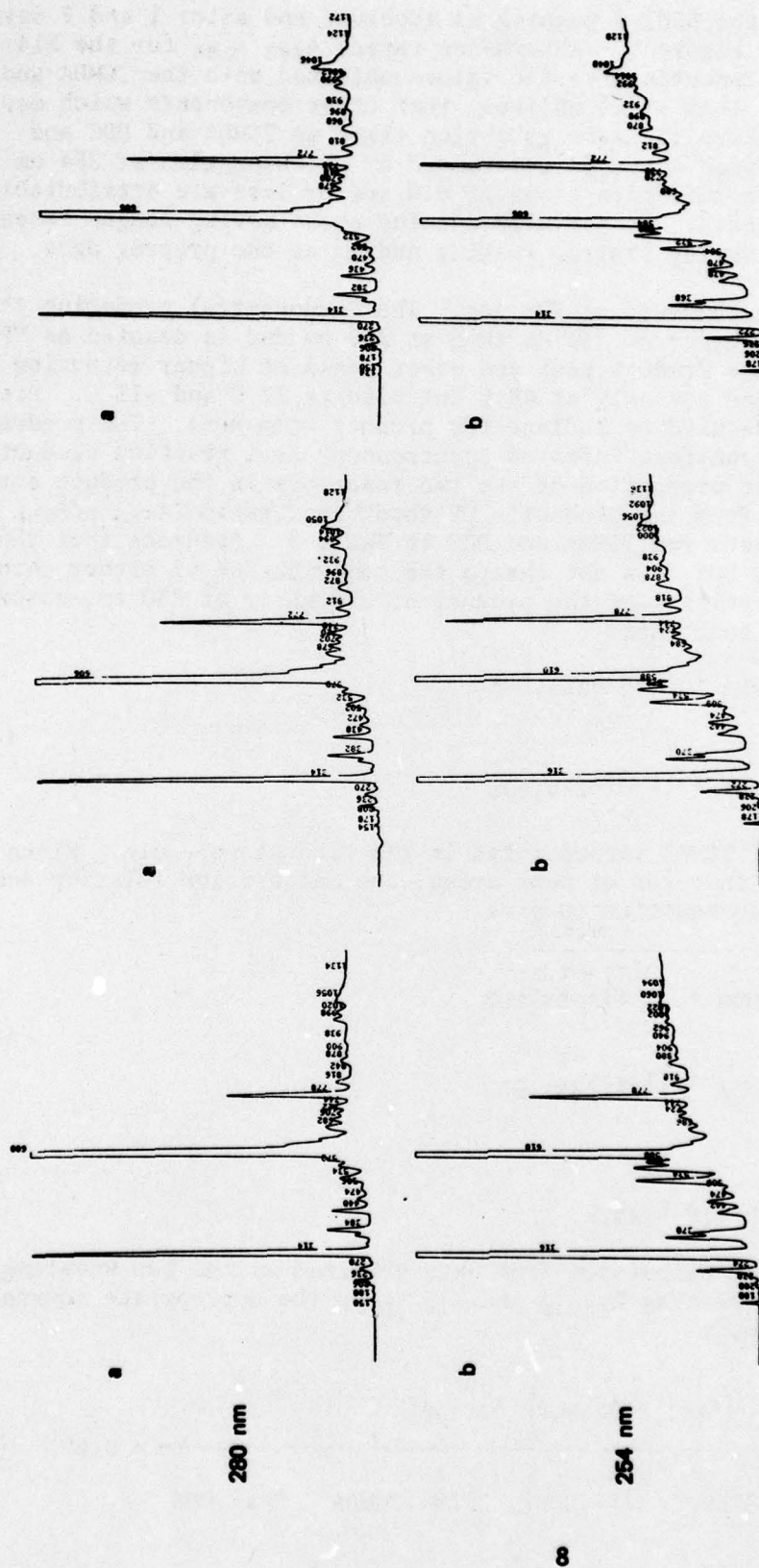


Figure 5. HPLC analysis of prepreps with UV detection at 280 nm and 254 nm.

The calculated x is near the theoretical value of $2/3$ which suggests that the ratio of TGMDA to DDS in the Product is 2:1. Using the theoretical value for x in Eq. 4, calibration constants for the Product are evaluated at 254 nm and 280 nm (Table 3).

The amounts (% wt) of TGMDA, DDS, and Product in the prepreg resin are reported in Table 4 as a function of aging time at different temperatures. The values at -13 C and 22 C were determined from data obtained with UV 254 nm detection. Both 254 nm and 280 nm detection were used to obtain the 49 C data. At least six experiments were run to evaluate the standard deviation of each value at -13 C and 22 C. There are at least three significant sources of error: (i) the assumption of uniform fiber density; (ii) reproducibility of injections; and (iii) proper integration of peak areas. For the prepreg and sample size considered in this study, the assumption of uniform fiber density was valid. Analyses of sections from different panels generally gave average results which agreed within $\pm 2\%$. An error or about 2% was introduced by failure to exactly reproduce injection volumes. No significant error was contributed by the integration of the TGMDA peak; however, in certain instances as much as 5% error may have resulted in the analysis of DDS due to the contribution of unresolved peaks near the baseline.

Data in Table 4 are plotted in Figures 6 and 7. At 22 C, a sharp decrease in TGMDA and DDS occurs within the first week of aging. About 20% to 30% of the TGMDA and DDS initially present disappears during this period with the DDS being consumed slightly faster than TGMDA. Initially, TGMDA and DDS represent 64.3% wt of the prepreg resin, but after 53 days their contribution is only 38.2% wt - a difference of 26.1% wt. Although "Product" is the major reaction product analyzed by HPLC, it accounts for only 3.57% wt or about 14% of this difference. Therefore, it is likely

Table 4. HPLC ANALYSIS OF 3501-6 PREPREG AGING*

T (°C)	t	Percent by Weight		
		TGMDA	DDS	Product
- 13	0	39.8 \pm 1.0	24.5 \pm 0.2	1.57 \pm 0.02
	7 days	39.7 \pm 0.8	23.9 \pm 0.9	1.65 \pm 0.02
	41 days	38.1 \pm 1.2	23.3 \pm 0.8	1.62 \pm 0.16
	7 months	36.9 \pm 1.2	19.6 \pm 0.6	2.1 \pm 0.3
	10 months	34.1 \pm 1.0	19.8 \pm 0.1	4.6 \pm 0.6
22.0 \pm 0.5	1 day	37.6 \pm 0.9	22.8 \pm 0.7	1.59 \pm 0.11
	4	34.5 \pm 0.9	18.1 \pm 0.8	1.72 \pm 0.06
	6	30.5 \pm 0.8	18.1 \pm 0.8	1.94 \pm 0.06
	15	28.6 \pm 1.0	16.5 \pm 0.7	2.73 \pm 0.12
	28	26.3 \pm 0.8	15.9 \pm 0.6	3.67 \pm 0.11
	33	25.7 \pm 1.0	14.6 \pm 0.8	3.79 \pm 0.13
	53	25.1 \pm 0.6	13.1 \pm 0.4	5.14 \pm 0.15
49 \pm 2	4 hours	34.8 (35.3)	20.0 (20.2)	6.6 (5.4)
	8	34.9 (35.7)	20.3 (20.3)	6.7 (6.3)
	16	32.8 (33.9)	18.1 (18.6)	6.2 (6.1)
	1 day	29.5 (36.7)	18.1 (19.4)	7.1 (7.1)
	2	30.0 (31.6)	16.7 (16.3)	8.1 (8.4)
	3	27.0 (28.3)	14.7 (13.8)	7.6 (7.0)
	4	25.1 (25.7)	13.3 (12.3)	7.9 (8.2)
	7	21.3 (21.8)	8.3 (7.6)	10.8 (8.4)

*Percent weight data in parenthesis were obtained using UV 280 nm detection.

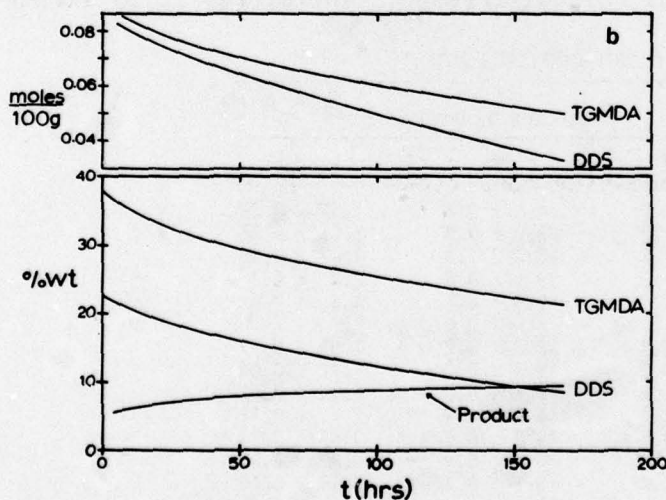
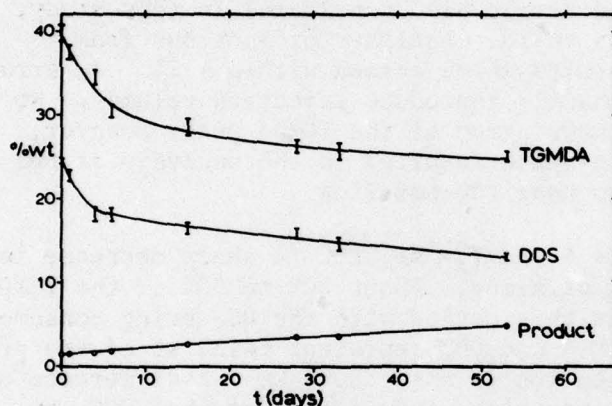
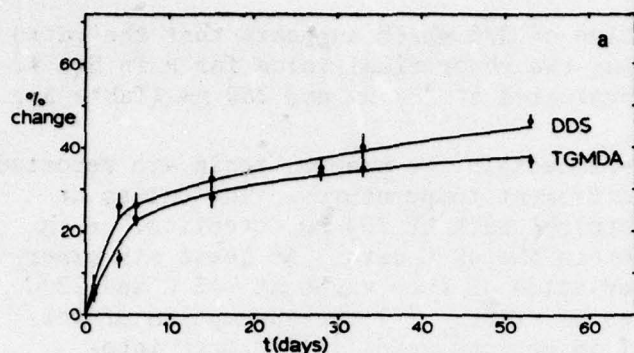


Figure 6. Changes in chemical composition of resin during prepreg aging at (a) 22 C and (b) 49 C.

that a host of products are being formed not only between TGMDA and DDS, but also between DDS and other epoxides as well as higher oligomers of TGMDA. The effects of epoxy addition reactions, hydrolysis, and oxidation should also be considered. The large number of poorly resolved peaks with high retention times attest to the variety of products formed during aging and to their relatively high polarity.

Similar changes in TGMDA, DDS, and the Product occur at 49 C but much faster than at the lower temperatures. After 1 week, half the TGMDA and DDS initially present is consumed. The plot in Figure 6b of TGMDA and DDS in moles per 100 grams of prepreg resin indicates that DDS is disappearing at a rate nearly 30% higher than TGMDA. Most likely, the higher apparent rate of DDS consumption results from its reaction with epoxides other than TGMDA.

To illustrate the effects of aging time and temperature, the TGMDA and DDS are plotted versus the logarithm of aging time in Figure 7. The dashed lines indicate the weight percentages of TGMDA and DDS at which the prepreg is considered no longer acceptable for processing. The positions of the dashed lines were determined from TTW readings which have been correlated with prepreg processability.² According to this correlation, the 3501-6 prepreg becomes unacceptable when the levels of TGMDA and DDS in the prepreg resin drop below 28% wt and 16% wt, respectively.

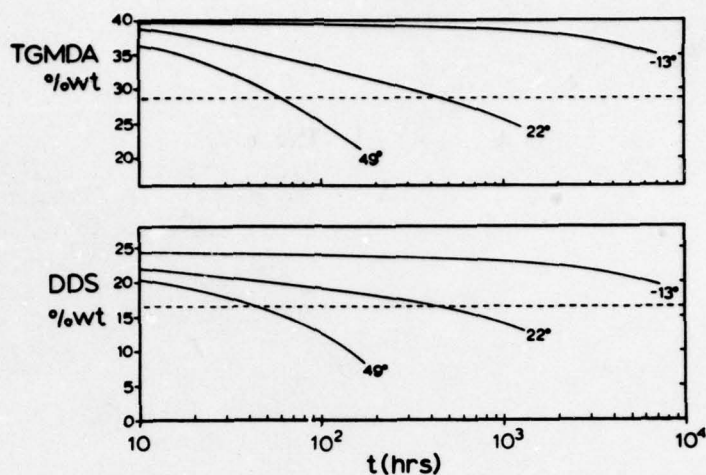


Figure 7. A comparison of changes in prepreg composition at different temperatures.

CONCLUSION

An HPLC method has been developed for the quality control of 3501-6 prepregs. Normal phase adsorption chromatography with gradient elution not only fingerprints the chemical composition of the prepreg resin but also enables the curing agent DDS and the principal epoxy component TGMDA to be quantitatively analyzed. The amounts of TGMDA and DDS are found to decrease with prepreg aging. Since processability is related to the chemical composition of the prepreg, the HPLC method may be applied both as a standard test method in Military Specifications to certify prepreg acceptability and as a method for process control. Conceivably, the information obtained from an HPLC analysis could be used to adjust processing conditions to optimize the properties of the composite being produced.

A variety of reaction products may form during aging and their formation is suggested in the HPLC analysis by the large number of peaks which appear at high retention times and grow as the prepreg ages. A major product is found to consist of 2 parts TGMDA to 1 part DDS.

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